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CONTRIBUTION FOR:

ELECTRONIC ENCYCLOPEDIA OF REAGENTS FOR ORGANIC SYNTHESIS

ADAMANTANETHION

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Adamantanthion

Formula (**1**)

[23695-65-0] $C_{10}H_{14}S$ (166.29)

(reagent used as a stable thioketone useful for the preparation of adamantyl substituted products[1] and for studies on the reactivity of thiocarbonyl compounds)

Alternate Name: Tricyclo[3.3.1.1^{3,7}]decan-2-thion

Physical Data: mp 173-174 °C (petroleum ether),[2] 164-166 °C,[3] 160-162 °C (sublimation).[4]

Solubility: soluble in almost all organic solvents; insoluble in water.

Form Supplied in: orange crystals, commercially not available.

Analysis of Reagent Purity: IR,[2] ^{13}C-NMR.[5]

Preparative Methods: the most frequently applied method to prepare the title reagent is the thionation of adamantanone with P_4S_{10} in pyridine.[2,6,7] Other thionation reagents such as $[(C_6H_{11})_3Sn]_2S$[8] or $(Me_3Si)_2S$[9] as well as H_2S in the presence of *p*-toluene sulfonic acid[10] are also used. Treatment of adamantanone with H_2S/HCl in ethanolic solution at –55 °C affords the hemithioacetal, which decomposes at 100-130 °C/15-100 Torr to yield **1**.[2]

Purification: column chromatography (silica gel, petroleum ether/dichloromethane); sublimation.[4,11]

Handling, Storage, and Precautions: camphoraceous odor; stable at low temperature (dry ice) under inert gas, decomposes slowly at room temperature in contact with air; safe in handling.

Conversion to Adamantanone

The reaction of **1** with nitrosonium tetrafluoroborate ($NO^+BF_4^-$) in dichloromethane at rt leads to adamantanone (**2**) (eq 1).[12] Treatment of **1** with clay-supported cupper nitrate ($Cu(NO_3)_2$) under similar conditions gives **2** in 68 % yield.[13] Formation of **2** (40 %), together with other products, is also reported to occur by ozonolysis in dichloromethane at –70 °C.[14]

eq (1)

Heating of **1** in ethanol in a sealed tube at 80 °C for 14 h yields, after chromatographic workup (SiO_2, hexane/benzene 10:1), **2** as the major product (67 %) along with di(adamantan-2-yl)-disulfane (20 %).[15] The formation of **2** is also observed when the [2+3] cycloadducts of **1** with nitrile oxides are heated to 185-250 °C.[16] Similar treatment of the cycloadduct with diphenyl-nitrile imine leads to adamantanylidene *N*-phenylamine, which can be hydrolyzed in aqueous HCl to give **2**.[16] Hetero-Diels-Alder reaction of **1** with α,β-unsaturated aldehydes and ketones carried out in benzene at 80 °C in the presence of 1,4-hydroquinone afford variable amounts of **2**

in addition to the dimer **3** and the corresponding [2+4] cycloadducts as the major products.[15] The latter, being mixed thioacetals, undergo smooth hydrolysis in aqueous ethanolic solution to yield **2**.

Dimerization and Trimerization

Dimerization of **1** leading to 1,3-dithiethane **3** (68 %) occurs smoothly in methane sulfonic acid at rt (eq 2).[2,7] The dimer **3** is formed as a minor product in attempted hetero-Diels-Alder reactions of α,β-unsaturated ketones with **1** in the presence of hydroquinone at 180 °C.[15] The dimer **3** appears as the major product when a mixture of **1** and 2-(hydroxymethyl)- or 2-[(*N*,*N*-dimethylamino)methyl]phenols in xylene are heated at 180 °C in the presence of catalytic amounts of 1,4-hydroquinone.[17] Reaction of **1** with PCl_5 in boiling tetrachloromethane leads to the dimer **3**.[18] The same product is formed by direct irradiation (λ = 254 nm or > 420 nm) as well as when sensitized with benzophenon.[19]

eq (2)

The trimer **4** is obtained from **1** upon treatment with methane sulfonic acid diluted in diethyl ether at rt (eq 2).[2] Its formation is also reported when a solution of **1** in dichloromethane is stirred in the presence of silica gel.[18] The main product of this reaction is dispiro[1,2,4-trithiolane-3,2':5,2"-diadamantane].

The structures of the dimer **3** and the trimer **4** have been established by X-ray crystallography.[18] Thermal decomposition of **4** at 350-355 °C leads to the momomer **1.**[2]

Reduction Reactions

Adamantane-2-thiol (**5**) can be conveniently prepared by the reduction of **1** with sodium borohydride in DME solution (eq 3).[20] The formation of **5** is also reported to occur in reactions of **1** with organolithium compounds[21] and with Grignard reagents.[22]

eq (3)

Oxidation Reactions

A straightforward procedure for the conversion of **1** in adamantanethione *S*-oxide (adamantanyl-idene sulfine) (**6**) is using *m*-CPBA in diethyl ether (eq 4).[23] Other procedures to oxidize **1** using dimethyldioxirane in acetone[24] or oxone® in a two-phase system[14] are less efficient. Sulfine **6** is not only a superior dipolarophile[23,25,26] but also reacts with cycloaliphatic thioketones as a 1,3-dipolar species.[27]

eq (4)

Sulfur Transfer Reactions

In numerous reports, **1** is shown to act as a potent interceptor of sulfur, leading to the reactive adamantanethione *S*-sulfide (adamantanylidene thiosulfine) (**7**).[28] This intermediate is believed to exist in equilibrium with the corresponding spirodithiirane **8**. In contrast to the relatively stable **6**, neither **7** nor **8** can be isolated (eq 5).

eq (5)

However, **7** is a reactive 1,3-dipole, which undergoes [2+3] cycloadditions with thiocarbonyl compounds to yield 1,2,4-trithiolane derivatives. For example, heating of **1** and elemental sulfur in xylene leads to the trithiolane **9** (eq 6).[29] The same reaction can be performed in toluene/-trichloromethane solution.[30] Reaction of **1** with S_8 in the presence of sodium thiophenolate in acetone affords **9** as a minor product, along with 1,2,4,5-tetrathiane (**10**) and small amounts of 1,2,3,5,6-pentathiepane (**11**) (eq 6).[31] After a reaction time of 7 h, **11** is the major compound of the reaction mixture (78 %). Unexpectedly, **9** is also formed in good yield (69 %) on treatment of a solution of **1** in abs. THF with a catalytic amound of TBAF[32] as well as in the presence of silica gel in dichloromethane solution.[18]

eq (6)

The formation of **9** is also observed when **1** reacts with aniline in benzene solution at rt. Moreover, in the analogous reaction with *p*-toluene sulfonamide in dioxane, the formation of **9** is accompanied by trimerization and dimerization of **1** to give **4** and **3**.[33]

Reactions with Chlorine and Chlorosulfanes

Chlorine adds smoothly to the C=S group of **1** leading to α-chlorosulfanyl chloride **12** (eq 7).[34] Analogously, sulfur dichloride converts **1** in the chlorodisulfane (**13**). The reactions of **1** with the stable α-chloro chlorosulfanes (**14**) afford the non-symmetrical di- and trisulfanes (**15**) (eq 7).[35]

eq (7)

Addition Reactions with Organometal Compounds

Nucleophilic additions of organometal compounds with thiocarbonyl groups are known to occur in a thiophilic or carbophilic fashion.[36] The type of the product formed depends on the reagent and on the solvent. For example, prenyl lithium adds to **1** in a carbophilic manner to give the corresponding thiol, which is converted to the stable methyl thioether (**16**) by treatment with methyl iodide.[21] By contrast, the reaction of **1** with butyllithium in THF gives, after acidic work-up, mainly adamantanethiol (**5**) and small amounts of (adamantan-2-yl)(butyl)sulfane (**17**) as the product of the thiophilic addition.

Formulae (**16**)-(**19**)

The addition of methyl magnesium bromide with **1** yields different products dependent on the solvent used: whereas in THF thiophilic addition leads to **18**, the reaction in diethyl ether occurs via the carbophilic addition to give **19**.[22] In the reaction of vinyl magnesium bromide, the formation of a thiol resulting from carbophilic addition is reported.[22] The same addition mode is observed when propargyl magnesium bromide is used (eq 8). In this case, the initially formed product **20** partially cyclizes to give the spirocyclic dihydrothiophene (**21**).[22]

eq (8)

On the other hand, the analogous reaction with allyl magnesium bromide leads to (adamantan-2-yl)(allyl)sulfane exclusively.[22] As a plausible interpretation of different results observed with allylic reagents, i.e. carbophilic versus thiophilic addition, a subsequent [2,3] sigmatropic rearrangement is discussed.[21,37]

Carbophilic additions with **1** are reported for lithiated reagents, which are prepared *in situ* by deprotonation of activated CH compounds with butyllithium in THF. For example, the lithiated (methyl)(*p*-tolyl)sulfone reacts with **1** and, after treatment with methyl iodide followed by elimination of methanethiol, gives an (adamantylidenemethyl)(*p*-tolyl)sulfone.[38]

Treatment of 2,6-dimethylpyridine (**22**) with butyllithium in THF at –80 °C and subsequent addition of two equivalents of **1** leads to the dithiol **23** in 65-70 % yield (eq 9).[39] In this case, the formation of the new C,C bonds is observed as the exclusive process (carbophilic addition).

eq (9)

Deprotonation of (trimethylsilyl)diazomethane with butyllithium at –60 °C leads to a carbanionic species (**24**), which adds to **1**. In diethyl ether, two-fold extrusion of sulfur and nitrogen gives the olefinic product (**26**), isolated by distillation (8 %) (eq 10).[40] On the other hand, the reaction carried out in THF leads to the 1,2,3-thiadiazole derivative **26** (31 %).[40] The formation of these two products is rationalized by a carbophilic addition of the anion followed by elimination processes leading to **25** or cyclization yielding **26**.

eq (10)

Reactions with Carbenes

Photolysis of a mixture of **1** and diazomethane in an argon matrix at 10 K affords adamantane-thione *S*-methylide (**27**) as the product of the thiophilic attack of methylene (eq 11).[41] The structure of **27** in the matrix is evidenced by spectroscopic methods and by calculations. The ylide **27** undergoes a 1,3-dipolar electrocyclization at ca. 80 K to yield the stable spirothiirane

(**28**). The formation of other thiocarbonyl ylide derivatives of **1** in photochemical reactions of aromatic diazo compounds, such as diphenyl diazomethane and 9-diazofluorene, are also reported.[42] Similarly, the oxocarbene generated by photo-rearrangement of benzocyclobutene-dione is trapped by **1**.[43]

eq (11)

Strongly electrophilic dihalocarbenes add easily to **1** leading to the corresponding *gem*-dihalogenated thiiranes. Dichlorocarbene can be generated conveniently either by thermal decomposition of (trichloromethyl)phenyl mercury (Seyferth reagent) or by elimination of hydrogen chloride from trichloromethane in a two-phase system (Makosza reaction).[44] Unlike other halogenated thiiranes, the corresponding derivative of **1** is a fairly stable compound.

The nucleophilic dimethoxycarbene can be conveniently generated by thermal decomposition of the 1,3,4-oxadiazole derivative (**29**) at 100 °C.[45] When the decomposition is carried out in toluene in the presence of **1**, dimethoxythiirane (**30**) is produced in 92 % yield (eq 12).[46] The latter is smoothly desulfurized by treatment with triphenylphosphane to give the ketene acetal (**31**).

eq (12)

The spirocyclic thiirane (**28**) is also available by methylene transfer from triphenylphosphonium methylide (Wittig reagent) to **1**.[47] An improved protocol for the isolation of **28**, using carbon disulfide as a solvent and an excess of elemental sulfur, is published.[48]

Formation of Thietanes

The reaction of cycloheptatrienyl carboxylic acid chloride (**32**) and **1** in benzene in the presence of triethylamine gives a mixture of the two products **33** and **34** in 20 und 69 % yield, respectively (eq 13).[49] The structure of thietane **33** formally corresponds to the [2+2] cycloadduct of **1** and the ketene, which is generated from **32** *in situ*. The formation of **34** is an evidence for a zwitterionic intermediate, in which the ring closure to **34** competes with the cyclization to **33**.

eq (13)

Thietanes (**36**) are formed regioselectively when mixtures of **1** and ketene acetals of type **35** are irradiated in pentane solutions (eq 14).[50] In the case of the dimethylketene acetal, a mixture of two regioisomeric thietanes is formed.

eq (14)

Irradiation ($\lambda > 420$ nm) of a solution of **1** and α-methylstyrene in benzene affords a mixture of thietane (**38**) and (adamantan-2-yl)(2-phenylallyl)sulfane (**39**) (eq 15).[19] The key intermediate in this reaction is the diradical (**37**), which cyclizes to give **38** or undergoes a 1,5 hydrogen shift to yield **39**.

eq (15)

[2+3] Cycloadditions

Diazo Compounds

Diazomethane reacts with **1** at low temperature to give a mixture of the two regioisomeric [2+3] cycloadducts (**40**) and (**41**) (eq 16).[51,52] The ratio of the products depends on the polarity of the solvent. Whereas in aprotic, non-polar solvents 2,5-dihydro-1,3,4-thiadiazole (**40**) is the main product, the reaction in methanol results in a 1:9 mixture of **40** and **41**, in favor of the 4,5-dihydro-1,2,3-thiadiazole (**41**).[53] Both adducts can be isolated and used for further reac-ions.[48,54,55] Thermolysis of **41** in boiling xylene yields thiirane (**28**) as the main product together with homoadamantanethione and small amounts of methylenadamantane. The isomer **40** extrudes nitrogen much easier in a cycloreversion leading to the intermediate adamantanethione *S*-methylide (**27**), which undergoes easily [2+3] cycloadditions with a variety of electron-deficient C,C- and C,X double bonds.[56-59].

eq (16)

The analogous reaction of **1** with diazoethane affords regioselectively the cycloadduct of type **40**, which can be isolated.[16,60] The reaction with phenyldiazomethane occurs slower, and at rt spontaneous evolution of nitrogen takes place leading to a phenyl derivative of the thiirane (**28**) via the corresponding thiocarbonyl ylide.[16]

Sterically hindered diazocompounds react with **1** to give stable, crystalline cycloadducts, which eliminate nitrogen at elevated temperature to yield thiiranes.[61,62] By treatment with triphenyl-phosphane, the latter are converted in sterically congested olefins[61] (two-fold extrusion reaction).[63] As an example, the reaction sequence with di(*tert*-butyl)diazomethane is shown in eq 17 (→ **42** → **43** → **44**).

eq. (17)

Diphenyldiazomethane and 9-diazofluorene react with **1** in boiling THF to yield the correspond-ing thiiranes, which are desulfurized in a one-pot procedure to give the aryl-substituted olefins.[64] A kinetic study of the reaction of **1** with diphenyldiazomethane in DMF at 40 °C is reported.[65]

Ethyl diazoacetate in THF at rt reacts slowly with **1**. The initially formed cycloadduct releases nitrogen spontaneously, and the intermediate thiocarbonyl ylide (**45**) intercepts **1** yielding 1,3-dithiolane (**46**) by a regioselective [2+3] cycloaddition (eq 18).[66] The reaction is accelerated by

addition of catalytic amounts of lithium perchlorate.[66] The same product **46** is formed when a solution of dimethyl bromoketene acetal and **1** in pentane is irradiated with light of the wavelength $\lambda > 400$ nm.[67]

eq (18)

The reaction of **1** with α-diazoketones (**47**) in toluene at 90 °C occurs with evolution of nitrogen. The carbonyl-functionalized thiocarbonyl ylide (**48**) undergoes a 1,5-dipolar electrocyclization[68,69] to give spirocyclic 1,3-oxathiols (**49**) (eq 19).[70,71]

eq (19)

Similar reactions of **1** with α-diazoamides in THF require catalysis with lithium perchlorate. Depending on the substituent at C(α) of the starting material, the 1,5-dipolar electrocyclization competes with the 1,3-dipolar ring closure to give the thiirane.[72]

Heating of a three-component mixture consisting of **1**, dimethyl fumarate, and phenylazide in neat leads to the 1,3-oxathiol derivative (**52**), which results from a reaction cascade.[73] The first step of this conversion is the [2+3] cycloaddition of phenyl azide to methyl fumarate and subsequent isomerization of dimethyl 4,5-dihydro-1*H*-1,2,3-triazole-4,5-dicarboxylate to the α-diazoester (**50**). Subsequent reaction with **1** and elimination of nitrogen leads to the highly

functionalized thiocarbonyl ylide (**51**), which, after 1,5-dipolar electrocyclization and further transformations, yields (**52**) (eq 20).

eq (20)

Organic Azides

Organic azides react with **1** at 80 °C under evolution of nitrogen and, along with adamantanylidene amines (**56**), 1,2,4-trithiolane (**9**) is always the second product.[74,75] In these reactions, adamantanethione *S*-imides (**54**), which are generated by nitrogen elimination from the initially formed 1,2,3,4-thiatriazole (**53**), are believed to be key intermediates (eq 21). They undergo ring closure to yield thiaziridines (**55**), which are efficient sulfur donating species by forming imines (**56**). The interception of the sulfur atom by **1** converts it into the reactive thiosulfine (**7**), which undergoes a [2+3] cycloaddition with **1** to give **9**.

eq (21)

In a three-component reaction with **1**, phenyl azide, and fumaronitrile, the formation of **9** is a dominant process, and neither the intermediate *S*-imide (**54**) (R = Ph) nor thiosulfine (**7**) are intercepted.[76]

Nitrile Oxides

Differently substituted nitrile oxides (**57**), which are geneated *in situ* by base catalyzed elimination of hydrogen chloride from *N*-hydroxy imidoyl chlorides, in the presence of **1** undergo smoothly [2+3] cycloadditions to yield 1,4,2-oxathiazole derivatives in a regioselective manner.[16,77] An example with benzonitrile oxide is presented in eq 22.

eq (22)

The cycloadducts of type **58** decompose while heated to 185-250 °C to give the corresponding isothiocyanates and adamantanone (**2**).

Kinetic studies on reactions of substituted adamantanethiones with nitrile oxides are reported.[78]

Nitrile Imides

Similar to the reactions with nitrile oxides, nitrile imides (**59**) undergo regioselective [2+3] cycloadditions with **1** yielding spirocyclic 4,5-dihydro-1,3,4-thiadiazoles (**60**) (eq 23).[16,77] Thermal decomposition of these cycloadducts at 200 °C leads to (adamantanylidene)(phenyl) amine and aryl nitrile.

eq (23)

Nitrile Sulfides

Aromatic nitrile sulfides (**62**), which are generated by thermal decarboxylation of 1,3,4-oxathiazol-2-ones (**61**) in boiling xylene, can be trapped by **1** to give the 1,4,2-dithiazole derivatives (**63**) in moderate yields (eq 24).[29] The reaction is accompanied by sulfur transfer to **1** and subsequent formation of 1,2,4-trithiolane **9**.

eq (24)

Nitrones

Cyclic and acyclic nitrones are reported to undergo [2+3] cycloadditions with **1**. Typically, the reactions are carried out in toluene or trichloromethane solutions at rt.[3,79,80] For example, nitrone (**64**) and **1** react to give **65** in 74 % yield (eq 25).[80] When dissolved in $CDCl_3$, **65** dissociates to **1** and **64**, and an equilibrium is established proved by ^{1}H-NMR spectroscopy.[80]

eq (25)

Azomethine Ylides

Thermal ring opening of *N*-substituted aziridines is a convenient method for the generation of azomethine ylides in a stereoselective manner.[81] For example, dimethyl 1,3-diphenylaziridine-

2,2-dicarboxylate (**66**) in boiling toluene, is in equilibrium with azomethine ylide (**67**), which can be intercepted by **1** in a regioselective [2+3] cycloaddition to give **68** in 82 % yield (eq 26).[82-84]

eq (26)

Fluoride catalyzed desilylation of properly substituted (trimethylsilyl)methyl amines or (trimethylsilyl)methyl ammonium salts is a superior method for *in situ* generation of azomethine ylides.[81] The polycyclic adduct (**70**) is formed in 87 % yield when **69** is desilylated in the presence of **1** in dichloromethane solution (eq 27).[85]

eq (27)

1,3-Thiazolidines with unsubstituted C(2) and C(4) positions can be obtained from **1** and azomethine ylides without substituents at carbon atoms.[86,87]

Thiocarbonyl Ylides

Thermal decomposition of 2,5-dihydro-1,3,4-thiadiazoles is a convenient procedure for the generation of thiocarbonyl ylides under mild conditions (–30 to 45 °C).[58,59] Cycloaliphatic precursors (**71**) heated to 45 °C eliminate nitrogen and the illusive thiocarbonyl ylides (**72**) react with **1** to give regioselectively 2,5-dispiro-1,3-dithiolanes **73** (eq 28).[55,57,88,89]

eq (28)

The [2+3] cycloaddition of **1** with thiobenzophenone *S*-methylide can be performed at –30 °C and, in contrast to the above mentioned reactions with **72**, the sterically more hindered regio-isomer (**73**) is formed, accompanied by small amounts of 4,4,5,5-tetraphenyl-1,3-dithiolane (eq 29).[90] It is worth mentioning that the reaction of thiobenzophenone with **27** (generated from **40**) furnishes a mixture of almost equal amounts of the two regioisomeric cycloadducts (**73**) and (**74**).

eq (29)

Thiocarbonyl S-*sulfides*

Reactions of **1** with thiocarbonyl *S*-sulfides yield 1,2,4-trithiolanes, and the presence of the spiro-adamantane residue enhance the stability of these heterocycles significantly. For example, heating of a mixture of **1** and the thermolabile 2,2,5,5-tetraphenyl-1,2,4-trithiolane (**75**) in trichloromethane leads to the mixed trithiolane **76** in 81 % yield (eq 30).[91,92] An analogous conversion starting with 3,5-di(*tert*-butyl)-3,5-bis(4-methylphenyl)-1,2,4-trithiolane and **1** is also known.[93]

eq (30)

Three-membered sulfur heterocycles such as thiiranes and *in situ* formed thiaziridines are known as efficient sulfur donators. On the other hand, **1** is recognized as an excellent sulfur interceptor. Therefore, adamantanethione *S*-sulfide (**7**) is frequently postulated as an intermediate involved in the formation of 1,2,4-trithiolanes. The sulfurization of **1** with 2,2-diphenylthiirane yields the trithiolane-bis-spiroadamantane (**9**).[92]

Thermal three-component reactions with **1**, phenyl azide, and aromatic thioketones furnish mixtures of **9** and mixed 1,2,4-trithiolanes of type **76**.[74] These reactions are initiated by the [2+3] cycloaddition of phenylazide with the aromatic thioketone, being more reactive than **1**. The thiaziridine, which is formed after elimination of nitrogen, is considered as the sulfur donator according to the reaction sequence shown in eq (21).

The thermal stability of 1,2,4-trithiolanes containing a spiro-adamantane residue is confirmed by the experiment presented in eq 31.[94] The initial step of the reaction sequence is the formation of thiobenzophenone from (diphenylmethylidene)triphenylphosphorane and elemental sulfur at 110 °C.

eq (31)

Thiocarbonyl S-*oxides*

Cycloaliphatic thioketone *S*-oxides (sulfines) (**77**) react with **1** yielding 1,2,4-oxadithiolanes (**78**) as products of a [2+3] cycloaddition (eq 32).[95] These are the only examples in which sulfines act as 1,3-dipoles. On the one hand, the very high dipolarophilicity of thioketones ('super dipolarophiles') and, on the other hand, steric congestion are of crucial importance for the successful synthesis of **78**, which are obtained in almost quantitative yield.

eq (32)

Thiocarbonyl S-*imides*

Thiocarbonyl *S*-imides formed as intermediates in reactions of **1** with organic azides do not intercept **1** in the expected [2+3] cycloaddition,[74,75] in contrast to 2,2,4,4-tetramethyl-3-thioxocyclobutanone.[96] There is only one report of the reaction of **1** with the stable hexafluoro-thioacetone *S*-(adamantan-1-yl)imid (**79**).[97] In this reaction, carried out in deuterotrichloro-methane at 100 °C in a sealed tube, the trithiolane **9** is formed as the major product, and 1,4,2-dithiazolidine (**80**), an isomer of the expected [2+3] cycloadduct of **1** and **79**, is obtained in 8 % yield (eq 33). The formation of **80** can be explained by an isomerization of **79** to the correspond-ing thionitrone *via* a thiaziridine as the intermediate. This interpretation is supported by the formation of **9** in high yield.

eq (33)

Carbonyl Ylides

Heating of 3-phenyloxirane-2,2-dicarbonitrile (**81**) in toluene (110 °C) results in the ring opening leading to the reactive carbonyl ylide (**82**). The latter can be intercepted by **1** to give the 1,3-oxathiolane (**83**). The isomeric product (**84**) results from the nucleophilic ring opening of **81** by the sulfur atom of **1** and subsequent ring closure (eq 34).[98]

eq (34)

Carbonyl O-*oxides*

The ozonolysis of alkyl vinyl ethers of type **85** in diethyl ether or dichloromethane at –70 °C is an efficient method for *in situ* generation of carbonyl *O*-oxides (**86**), which belong to less explored 1,3-dipolar species. When the reaction is carried out in the presence of **1**, 1,2,4-dioxathiolanes (**87**) are obtained in up to 70 % yield (eq 35).[14,99] The [2+3] cycloaddition occurs regio-selectively.

eq (35)

Reactions with Oxiranes

Monosubstituted oxiranes undergo a *Lewis*-acid catalyzed reaction with **1** to give 1,3-oxathiolanes in moderate yield.[100] In the presence of zinc chloride in dichloromethane at –30 °C, the reaction with phenyloxirane occurs regioselectively to give the 4-phenyl-1,3-oxathiolane (**89**) (eq 36). Analogous reactions catalyzed with silica gel are performed with methyl- and phenyloxirane leading to mixtures of regioisomeric 1,3-oxathiolanes, e.g. **89** and **90**. Using enantiomerically pure oxirances, optically active products are obtained.

eq (36)

[2+4] Cycloadditions

Thermal cycloaddition reactions of **1** with conjugated, acyclic and cyclic dienes (hetero *Diels-Alder* reaction) in toluene at variable temperatures in the presence of 1,4-hydroquinone afford thiines of type **92** (eq 37).[77,101] For example, the reaction with *Danishefsky*'s diene (**91**) leads regioselectively to **92**, which, after desilylation, gives **93** in good yield. In the reaction with isoprene, two regioisomeric cycloadducts are formed in comparable amounts.

eq (37)

In analogous reactions, α,β-unsaturated carbonyl compounds and **1** at 80-140 °C give the expected 1,3-oxathiin along with small amounts of the dimer (**3**) and up to 38 % of **2**.[15,77]

A special case of heterodienes are *ortho*-quinone methanides of type **96**, which frequently are generated *in situ* by thermal 1,4-dehydration or 1,4-deamination of 2-(hydroxymethyl)phenols and 2-[(*N*,*N*-dialkylamino)methyl]phenols, respectively. When the precursors **94** or **95** are heated in xylene at 180 °C in the presence of **1** and catalytic amounts of 1,4-hydroquinone, the fused heterocycle **97** is formed (eq 38).[17,77]

eq (38)

The thermal ring opening of benzothiete leads to the sulfur analogue of **96**, which can be trapped by **1** to give the corresponding 1,3-benzothiin, i.e. the sulfur analogue of **97**.[102]

The formation of 1,3-oxathiin derivatives (**98**) and (**99**) is reported to occur when **1** reacts with acetylene carboxylic acids[103] or bis(pivaloyl)ketene.[104] The structures of the products are shown in eq 39.

eq (39)

Photochemical Reactions

Irradiation (λ = 470-500 nm) of a solution of **1** in benzene in the presence of equimolar amounts of adamantane-2-thiol (**5**) leads to the formation of the symmetrical di(adamantan-2-yl)disulfane.[105] When **1** is irradiated in hydrocarbons such as cyclohexane, neopentane, butane,

1,1,2,2-tetramethylcyclopropane, etc. with UV light (λ = 254 nm), mixtures of two isomeric adducts are formed, always accompanied by dimer **3**. A typical example leading to **100** and **101** is shown in eq 40.[106] These conversions are considered to occur *via* singlet π,π^* hydrogen abstraction leading to a radical pair.

eq (40)

Another example with trimethylsilane is described to give the silylated product (**102**) (eq 41).[107]

eq (41)

The absorption, emission, and excitation spectra of **1** are described in detail and compared with those of other thioketones.[108]

Miscellaneous

Recently, the reaction of **1** with Lawesson's reagent in refluxing deuteriotrichloromethane has been reported to yield spiro-1,3,2-dithiaphosphetane-2-sulfide (**103**) in 87 % yield (eq 42).[109] The structure of this formal [2+2] cycloadduct, which is a sulfur analogue of the postulated intermediates in the thionation of ketones with Lawesson's reagent, has been established by X-ray crystallography.

eq (42)

When heated above the melting point (163-165 °C), the colorless crystals turn to a purple oil indicating the decomposition to **1**.

Heating of a mixture of **1** and 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-germanonorbornadien (**104**), the precursor of dimethylgermylene, in benzene at 70 °C leads to the 1,3,2,4-dithiadigermolane (**105**) in 38 % yield, together with adamantylideneadamantane (**106**) and 1,2,3,4-tetraphenylnaphthalene (**107**) (eq 43).[110] A reaction mechanism via the formation of an intermediate thiagermirane is proposed.

eq (43)

The analogous three-membered intermediate can be trapped in the case of the 7,7-diphenyl-7-germanonorbornadien: after heating of a mixture with **1** in benzene to 80 °C, followed by treatment of the crude product with ethanol at rt, the 2-[(ethoxy)diphenylgermyl]adamantane-2-thiol is obtained in 50 % yield. The latter is believed to be the adduct of ethanol to the thiagermirane.

A thermally more stable thiagermirane (**109**) bearing bulky substituents can be isolated from the photolysis of a mixture of hexamesityltrigermane (**108**) and **1** in cyclohexane using a low-

pressure mercury lamp.[110] In addition of 53 % of **109**, 11 % of 1,2,3-thiadigermetane (**110**) and 37 % of the adamantanethione dimer (**3**) are obtained (eq 44). The photolysis and thermolysis of **109** leads to **1** and dimesitylgermylene, which can be intercepted by 2,3-dimethylbuta-1,3-diene. The photolysis of **109** in a hydrocarbon matrix at 77 K leads to the formation of the corresponding thiocarbonyl germide.[110]

eq (44)

A reduction of **1** to the mercuric thiolate (**112**) is achieved when a solution of **1** in acetonitrile is treated with bis(trifluoroacetato)-1,2-phenylenedimercury (**111**) in the presence of 1-benzyl-1,4-dihydronicotinamide (eq 45).[111]

eq (45)

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